



## Review

Recent advances in floating TiO<sub>2</sub>-based photocatalysts for environmental application

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## ABSTRACT

The light-harvesting and recycle of powder photocatalyst in suspended system are bottlenecks for high-efficient solar photocatalysis. Floating photocatalyst are highly sought-after and good candidates for practical environmental application due to the satisfaction with above requirements simultaneously. Over the past decades, floating TiO<sub>2</sub>-based photocatalysts have attracted much attention, which makes great progress and it is significant to review the recent advances. This review highlights the rational design and fabrication strategy for floating photocatalyst immobilized on various lightweight substrates (e.g. perlite, vermiculite, glass microbead, polymer, cork, expanded graphite) or self-floating photocatalyst. The special characteristics and deep understanding of photocatalytic mechanism for floating photocatalyst are summarized and discussed thoroughly. Moreover, the future research and challenge will focus on designing and optimizing the high-efficient broadband response floating photocatalyst to improve solar energy utilization. From an application viewpoint, floating photocatalyst have real practical applications in natural environment and are worthy of great attention.

## 1. Introduction

The past few decades have witnessed to huge development in industrialization bringing some problem at same time. Environmental pollutants have attracted more and more attention in the world [1,2]. Especially, water pollution becomes an urgent problem to be resolved, many scholars have studied how to treat wastewater from production and domestic [3]. But there are still many contaminants, in traditional sewage treatment process, which is difficult to be removed, for example, antibiotics [4,5], dyes [6,7], organic pesticides [8,9], polycyclic aromatic hydrocarbons (PAHs) [10,11] and so forth. To figure out this trouble, some new technologies are found [12], such as Fenton oxidation [13] and hybrid process combining several different kinds of processes treatment means (activated carbon, biofilm, enzyme reactors, etc.) [14], show a good ability to degrade organic pollutants and attract an increasing number of researchers [15]. However, in order to degrade pollutants, the excessive use of chemical reagents may do harm to the environment. With the development of science and technology, the semiconductor titanium dioxide (TiO<sub>2</sub>) as the representative of the photocatalytic technology is coming into horizon. Photocatalysis [16] as an alternative method has been used for degrading micro-pollutants in fields of environment.

It is the first time that Fujishima and Honda used semiconductor TiO<sub>2</sub> to photocatalytic decomposition of water in 1972 [17]. The mechanisms of photocatalytic oxidation of pollutants can be summarized in the following two steps [18]: (1) electrons, when the surface is exposure to ultraviolet light (UV) and visible light, transfer from the valence band to the conduction band [19]; (2) then valence band and conduction band show intense oxidizing and reducing respectively. In addition, hole oxidation is other oxidation mechanism. ·OH generating by the oxidation between hole and OH<sup>−</sup> can be usually considered as the “oxidizing agent”, further, oxidations occur “indirectly” by ·OH or “directly” by holes. The organic and inorganic contaminants in water are converted to harmless substances by oxidation-reduction property of photocatalyst [20,21]. Although the photocatalytic technique is a promising technology to remove the pollution from water, the amount of work has been done to settle this matter which limits the application of photocatalyst TiO<sub>2</sub> in industrial scale [22]: how to separate the photoinduced electron-hole pair [23]? how to improve the light utilization [24]? how to increase the recycle rate of photocatalyst? In recent work, several researchers used different methods [25] (doping ions, surface corrosion modification [26], mixing some chemical materials, etc.) to improve the performance of TiO<sub>2</sub> photocatalyst. Liu et al. [27] manufactured novel 3D mesoporous black TiO<sub>2</sub>/MoS<sub>2</sub>/TiO<sub>2</sub> nanosheets

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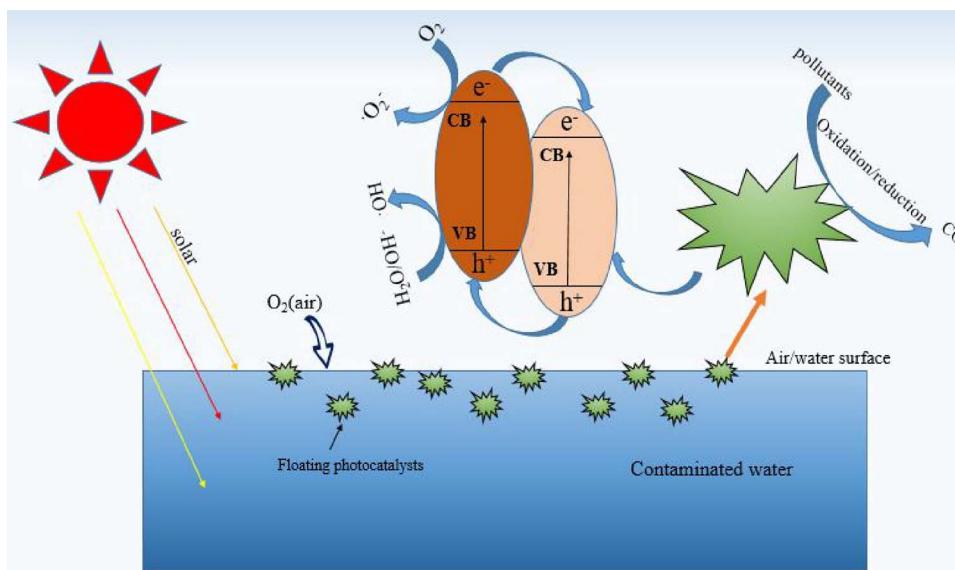


Fig. 1. Schematic depiction of the floating photocatalyst.

by a mechanochemistry method combine with an in-situ controllable solid-state reaction method. Although the activity, specific surface area and cycle had been enhanced by this means, the price and the quantity of  $\text{TiO}_2$  restricted its applications during wastewater treatment in industry [28]. In addition, the light utilization of  $\text{TiO}_2$  photocatalyst is fatal problem. As known, micropollutants, in  $\text{TiO}_2$  photocatalysis system, are degraded by photogenerated electrons and holes with redox ability on the photocatalyst surfaces. The energy of the incident photons matches or exceeds the bandgap of  $\text{TiO}_2$ , which result in photo-excitation of electron-hole pairs take place, subsequently, the pollutants are degraded [20]. However, the bandgap of  $\text{TiO}_2$  have decided to that only UV can be used, which have inhibited the light utilization. What is worse,  $\text{TiO}_2$  photocatalyst is distributed in the solution and precipitated into the water bottom, that resulting in lower light energy utilization because 20% of visible light and 1% of UV light can penetrate to underwater 0.5 m [29]. Obviously, it is huge threat to the generation of photogenerated electron-hole. In the other words, floating photocatalyst can yet be regarded as a promising choice to replace the traditional semiconductor  $\text{TiO}_2$  catalyst as shown in Fig. 1, on the basis of falling in between air and water surface, and the effective visible light utilization.

Floating  $\text{TiO}_2$ -based photocatalyst has been used to decompose oil, since 1993 [30], energy, time and cost have been attributed to study floating photocatalyst because of their unique characters. Floating photocatalysts, as the name implies, using lightweight material as carrier and/or self-floating, can float on the surface and shallow of water [30]. Just as some literatures reported [24,31], on one hand, floating photocatalyst takes advantage of illumination/light utilization when light is irradiated on the carrier, and based on the characters that it floats on the air-water interface, there is no need to stir, maximize the performance of photocatalyst and quantum utilization efficiency. On the other hand, contrasted with powder  $\text{TiO}_2$  system, floating photocatalyst decreases the cost of wastewater treatment because it is convenient to post-treatment, and get access to a large specific surface area too [32,35]. Meanwhile, due to unique structure of floating substance, floating photocatalyst minimizes loss of photocatalyst and avoided long-term contact between photocatalyst and pollutants which can decrease photocatalytic activity. Additionally, the problem of centrifugation is also critical and could be effectively solved by forming self-cleaning, anti-fouling and anti-bacterial film, immobilizing on poriferous sponge and modifying by magnetic particle, but those methods cannot enhance the visible light utilization of  $\text{TiO}_2$ . Furthermore, in floating photocatalytic system, the balance problem must be

considered among various factors, such as easy centrifugation, low-cost, low photocatalyst lost, high quantum utilization efficiency and direct combination with solar light. In view of the separation problems, which is difficult and necessary to separate photocatalyst on account of dispersing in the wastewater and doing some harmful impactions to our health respectively [30], the various carriers have been used to fixed carrier, such as perlite, vermiculite, glass, cork, graphite, polymer, as depicted in Fig. 2. Especially, floating photocatalyst has other preponderances. For example, the substrate of photocatalyst can be considered as the recycling of resources. Polystyrene (PS), the waste polymer can result in "white pollution", is one of the vital concerns to the environmentalists [33]. It is wise, sensible and advisable that the PS-supported floating  $\text{TiO}_2$  photocatalyst use waster PS to degrade even remove pollutants whether it is organic or inorganic, easily degradable or degradation-resistant [34].

Obviously, floating photocatalytic technology has unique advantage and is wroth further researching. Ang et al. [29] had reported an overview of immobilization of  $\text{TiO}_2$  onto supporting materials, and summarized photocatalyst supports, several technologies fixing  $\text{TiO}_2$  on the carrier and characterization of immobilized  $\text{TiO}_2$ . However, none of

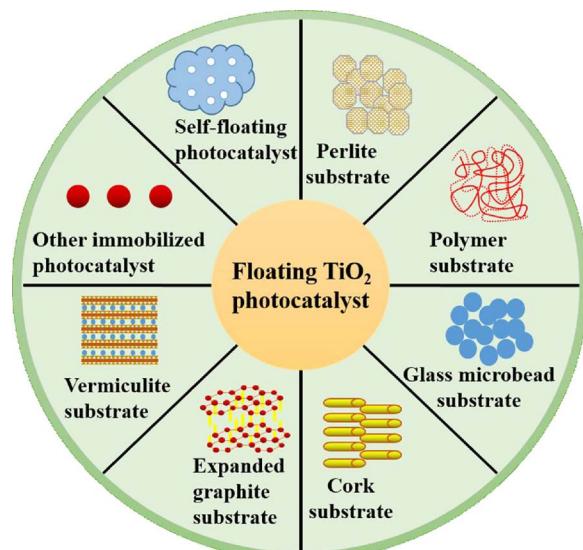


Fig. 2. Scheme of the floating  $\text{TiO}_2$ -based photocatalyst supports on different light-weight substrates and the self-floating photocatalyst.

the early literature detailed set forth floating photocatalyst from the aspect of fixed type. It is first time that the work focuses on floating photocatalyst no matter immobilized or non-immobilized, and elaborates the methods and supporters fabricating the floating photocatalyst. The advantage and disadvantage of floating photocatalysts have been analyzed. In order to speed up the process of industrialization of floating photocatalysts, numerous, significant and meaningful work is needed to enhance the performance of floating photocatalysts. Facing to the urgent water pollution problems causing by the toxic and micro-contaminants, it is significant that the application of floating photocatalysts in practical sewage treatment plant. Especially, due to the relatively high quantum utilization, less catalyst loss and lower operational cost of based on immobilized floating photocatalyst and self-floating photocatalyst, it is expected to play an important role in the process of photocatalytic degradation contaminants. In conclusion, it has great realistic significance for field related to photocatalysis, and is progressed for  $\text{TiO}_2$  photocatalyst application in practice.

## 2. Immobilized floating photocatalyst

### 2.1. Perlite substrate

Perlite is acid lava produced from volcanic eruption, which shapes a glassy rock through rapid cooling. It has its own name because of its pearlstone fissure structure. This particular type of glassy volcanic rocks contains  $\text{SiO}_2$  (greater than 60%),  $\text{Al}_2\text{O}_3$  (12–18%),  $\text{Na}_2\text{O}$  (5–10%),  $\text{K}_2\text{O}$  (2–5%) and others (<5%) [36,37], the numerous of micropores in the perlite ensure lightweight properties while providing the properties of thermal and sound insulation [38]. This natural alumino-silicate with extremely porous structure, excellent thermal and chemical stability provides a cheap and environment-friendly support for nanoparticles which immobilize on its surface [39]. Perlite can expand 10–30 times over its original volume if heated between 800 and 1150 °C because it contains 2–6% water in its structure [40]. Its unique characteristics of lightweight, sterile, insulating and fireproof make expanded perlite an excellent choice for many applications including construction, filtration, horticulture and insulation [41].

Unique structure determines that perlite can be used to floating carrier of the photocatalyst, it is first time that Hosseini et al. [42] proposed a new photocatalyst immobilizing the Degussa P25 on the granular perlite though coating process. Pieces of perlite can easily float on water surface due to its extremely low density, even after being coated with  $\text{TiO}_2$  particles, without being precipitated or suspended. Although the phenol degradation rate of  $\text{TiO}_2$ /perlite is less than that of  $\text{TiO}_2$ /glass, due to easier and less expensive operating conditions, perlite floating photocatalyst should also be taken into account for an industrial-scale treatment process. Subsequently, Xing et al. [43] prepared a highly porous  $\text{TiO}_2$  ceramic floating photocatalyst in Fig. 3A, with a camphene-based freeze-casting process and calcined. The perlite granules inside the porous  $\text{TiO}_2$  ceramic appeared to melt when the sintering temperature increased. The effect of 800 °C sintering temperature on rhodamine B (RhB) achieves a very high removal rate of 99.3% after 5 h. In recent years, perlite use in the thin film photoreactor has attracted considerable attention. Normally, a thin film of catalyst is usually attached to a fixed glass or metal slab which leads in a lower removal efficiency. However heterogeneous photocatalysis using floating substance catalysts is a good choice to solve this problem. Faramarzpour et al. [44] selected perlite as a support in a floating-bed photoreactor to degrade furfural. This floating-bed included 2–5 g perlite granules, which coated with  $\text{TiO}_2$ . Perlite is inert and erosion resistant, and it has a good surface area with an ability to keep the coated  $\text{TiO}_2$ , so that the  $\text{TiO}_2$  particles do not leave the perlite and act as suspended catalysts. Thus, light is irradiated in perlite surface without facing any barriers, the removal efficiency is up to 99.6%.

Apart from the removal of phenol, how to remove ammonia from industrial wastewater remains a big challenge. The separation progress

of the final products ( $\text{N}_2$  and  $\text{NO}_3^-$ ) that in a reduced costs and simplifies the wastewater treatment system seems to be difficult to eliminate. Shavisi et al. [45] firstly investigated the remove rate of ammonia by using floating photocatalyst immobilized  $\text{TiO}_2$  (P25) powder on perlite granules. When perlite granules are suspended in ammonia solution under UV irradiation, attributing to the synergistic effects between adsorption and photolysis, so the removal efficiency of ammonia can achieve 80%. Meanwhile, the separating nanoparticles after purification can be effectively solved when  $\text{TiO}_2$  nanoparticles are immobilized over perlite granules. Simultaneously, the preparation method also has certain influence on the floating photocatalyst. The impregnation method is simple, a lot of metals lead to the aggregation of active components. Unfortunately, it makes metal distribution non-uniform inside and/or outside the tunnel. Although the sol-gel method is complicated to operate, it makes  $\text{TiO}_2$  uniform distribution. So it is beneficial to improve the adsorption capacity of catalyst and increase photocatalytic active site. Wang et al. [46] had prepared doping  $\text{TiO}_2$ -pearlstone (PS) by sol-gel method to degrade diesel oil though the visible-light-driven photocatalysis. The lightweight PS can achieve the floatable of catalysts. Moreover,  $\text{SiO}_2$  is the main components of PS, which can efficiently enhance thermal stability of obtained photocatalyst. The result shows that B/N codoped  $\text{TiO}_2$ -PS exhibited excellent photocatalytic performance for diesel oil. The removal rate and  $k$  value of B/N cooped  $\text{TiO}_2$ -PS were 48% and  $0.08423 \text{ h}^{-1}$ , respectively.

Compared to perlite, expended perlite (EP) has the advantage of the relatively large grains, in the range of millimeters, can be easily separated from the reaction mixture. Many scholars and researchers have made a lot of efforts to research  $\text{TiO}_2$ /expended perlite. Dlugosz et al. [47] proposed a novel deposition route by direct hydrolysis of titanium (IV) isopropoxide in the presence of EP, in order to ensure four times higher loading rates and preserve the floating ability of EP. The catalyst showed good degradation of phenol. Xing et al. prepared a macro/mesoporous anatase  $\text{TiO}_2$  ceramic floating photocatalyst [48]. As shown in Fig. 4A, the expended perlite provided closed pores and maintained the floatability of the photocatalysts. Fig. 4D indicated that a total organic carbon (TOC) removal efficiency of 98.8, 98.6, 97.9, 98.5, and 98.0% could be achieved for octane, RhB, phenol, thiobencarb, and atrazine, respectively. Moreover, the prepared floating photocatalysts were easily recycled and retained high photocatalytic activity during reuse (Fig. 4B and C). Xue et al. [49] synthesized B-N- $\text{TiO}_2$ /expanded perlite floating photocatalyst with optimized mesoporous and high photocatalytic activity through a sol-gel synthesis. This  $\text{B}_{0.21}\text{N}\text{-}\text{TiO}_2/\text{EP}$  photocatalyst had large specific surface area ( $\sim 99 \text{ m}^2 \text{ g}^{-1}$ ). The size of photocatalyst particle was about 30–50 nm. The photocatalyst synthesizing through sol-gel method had a better Rh B degradation rate about 99.8% after 60 min (100 W Hg lamp). The photodegradation rate was up to 94% under visible light irradiation for 3 h.

According to the above research, the catalyst particles are suspended in the liquid, which makes it difficult to separate the catalyst from the liquid phase. At this point, the carrier which can float on the liquid phase should be needed, thus the photocatalyst can be better separation in the recycle and can be more fully exposed to light. The carrier must be corrosion resistant and prevent the catalyst from falling off during use, and obtain good support. So the perlite and expended perlite selected as the catalyst carrier is appropriate, it has many advantages, such as inert, high porosity, low density, natural abundance, the absence of toxicity and low price. Fig. 5 is floating reaction mechanism of photocatalyst, expanded perlite as a carrier of the catalyst can float on the water surface for long time, because it has cellular foam structure and has closed bottom shallow pits on the surface. The floating photocatalyst can effectively capture sunlight, meanwhile it can exposure in the air and contact with oxygen.

In summary, the perlite particles due to its unique characteristics are widely used in the field of floating photocatalysis and achieve promising degradation rates (Table 1). It can facilitate recovery in the

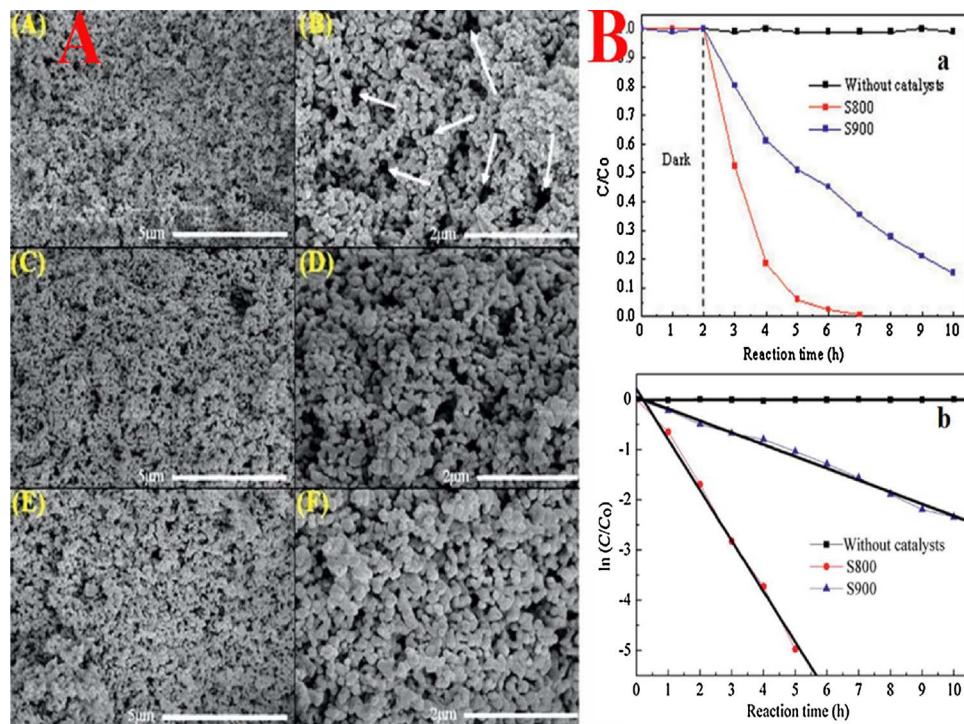


Fig. 3. SEM images (A) of the sintered bodies with 14.87 wt.% solid content slurries at sintering temperatures of (A, B) 800, (C, D) 900, and (E, F) 1000 °C. Time profiles (B) of the photocatalytic degradation of RhB (a), and Value of  $\ln(C/C_0)$  versus reaction time (b) with different catalysts and without a catalyst. Reprinted with permission from Ref. [43].

actual processing of treatment of pollutants, meanwhile it can float on the water and directly contact with light source. Simultaneously,  $\text{SiO}_2$  in the perlite can bond with  $\text{TiO}_2$  to form a strong  $\text{Ti}-\text{O}-\text{Si}$  bond. It also has other advantages such as low-priced, easily obtained, good light stability, strong oxidation ability and no secondary pollution. So the floating photocatalyst which the perlite acts as substrate has good commercial value and worth to further research. But they also have some disadvantages, the high water absorption makes it easy to demix. Thereby its performance will be greatly reduced and the physical state changes in everlasting treatment. So far, there are different techniques

for immobilizing  $\text{TiO}_2$  catalysts onto perlite or expended perlite, such as, spray coating, sol-gel methods, sputtering, and electrophoretic deposition. However, those techniques are not perfect due to the complex operation and weak bond between  $\text{TiO}_2$  and perlite, it is worth further investigating an effective, convenient, and simple immobilization technique. On the whole, perlite due to its very outstanding characteristics seems to be an ideal support for the immobilization of photocatalysts.

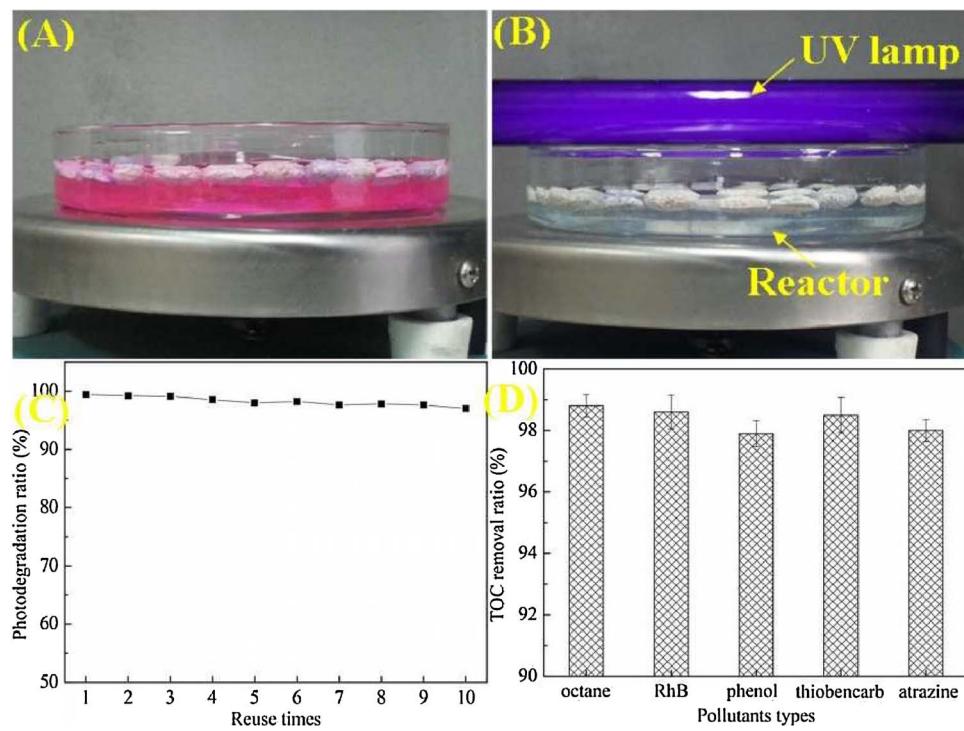


Fig. 4. Images of floating photocatalysts based on hierarchical porous  $\text{TiO}_2$  ceramic before (A), and after reaction (B), effect of floating photocatalyst cycle numbers (C) in  $10 \text{ mg L}^{-1}$  RhB degradation by S800, effect of floating photocatalysts on the TOC removal of  $10 \text{ mg L}^{-1}$  pollutants by S800 (D). Reprinted with permission from Ref. [48].

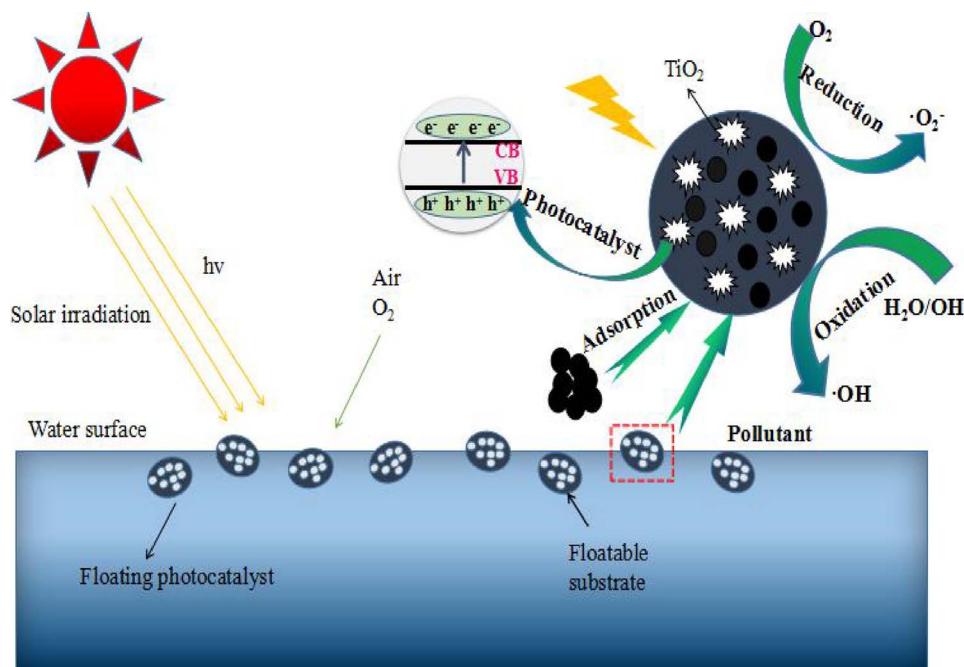


Fig. 5. Schematic depiction of the floating optimized photocatalyst of  $\text{TiO}_2$  coated on expanded perlite.

## 2.2. Vermiculite substrate

Vermiculite, which is a clay mineral enriched with Si and Al [50], is a natural and non-toxic mineral as well as belongs to silicate. And it is changed from biotite or phlogopite because of the weathering or hydrothermal alteration. When being heated, vermiculite expansion will occur and the size becomes 30 times as large as the original volume [51]. In fact, the purposes of vermiculite are very extensive such as insulating material, coating material, lightweight material and the application of high thermal resistivity [52]. Importantly, there is a tetrahedral-octahedral-tetrahedral layer lattice which is the basic structure composed of two silica tetrahedral sheet  $[\text{SiO}_4]$  coupled to another magnesium octahedral sheet  $[\text{MgO}_6]$  symmetrically in the vermiculite that is a 2:1 type of phyllosilicate [53]. And the water also exists as the water layers between the silicate layers so that the vermiculite has the process of dehydration-hydration when some conditions change (temperature, composition, pressure, relative humidity and size) [54].

Due to the layered structure of vermiculite, the performances of vermiculite are varied in adsorption, disorder effects, dehydration-hydration, isomorphic substitutions and expansion process [55]. Therefore, vermiculite has outstanding physical and chemical properties, especially expansion and dehydration-hydration are good for making it float on the water. Moreover, when vermiculite suffers sudden heating at high temperature, it will swell and form highly porous structure called expanded vermiculite (EV) [56]. Due to heat at high temperature in a short time, the water molecules in the layered structure change into steam, and the pressure formed by steam makes the slice open quickly

[57]. Hence, vermiculite expands to be a larger volume, meanwhile, there are many pores and a large number of air layers in the clearly layered structure. At this time, the relative density of vermiculite becomes smaller than water (the relative density of water is 1). Therefore, the expanded vermiculite can float on the water. And the mechanism of vermiculite expansion is shown in Fig. 6.

Unfortunately, vermiculite has strong absorbability after expansion or exfoliation. When vermiculite floats on the water, it can be considered as adsorbent for adsorbing organic contaminants and heavy metals owing to its high adsorption capacity [58]. Besides, expanded vermiculite not only has high specific surface area so that other molecules can interact with it, but also possesses large interlayer space to offer a suitable site for the chemical reactions of adsorbed organic pollutants in water [59,60]. Moreover, expanded vermiculite adsorbs water to form water layers between the silicate layers due to its property of dehydration-hydration. The quality and relative density of expanded vermiculite increase with the accumulation of organic contaminants and water adsorbed by expanded vermiculite. Therefore, expanded vermiculite will not always float on the water because of the absorbability which causes the relative density greater than water.

Hence, vermiculite has many outstanding properties so that it can be applied to some fields including industry and agriculture, but it still has some shortcomings that limit its development. So some modification methods are discussed, studied and applied to improve the properties of vermiculite, such as ion exchange, acid activation, pillaring and intercalation [53,59]. In particular, the expanded/exfoliated vermiculite has very high cation exchange capacity ( $120\text{--}150\text{ mol kg}^{-1}$ )

Table 1  
Summary of floating  $\text{TiO}_2$ -based photocatalyst with perlite substrate.

Catalyst	Weight	Light source	Target & concentration	Time	Removal efficiency	Refs.
$\text{TiO}_2$ /perlite	$11\text{ g L}^{-1}$	UV light	phenol $1\text{ mM}$	240 min	83.3%	[42]
porous $\text{TiO}_2$ ceramics	eighty pieces (20 mg each piece)	UV light	$\text{RhB } 10\text{ mg L}^{-1}$	300 min	99.3%	[43]
$\text{TiO}_2$ /perlite	3 g	UV light	furfural $0.5\text{ mM L}^{-1}$	120 min	99.6%	[44]
$\text{TiO}_2$ /perlite	11.70 g	UV light	ammonia $170\text{ mg L}^{-1}$	120 min	80%	[45]
B/N- $\text{TiO}_2$ -PS	$1.0\text{ g L}^{-1}$	visible light	diesel oil $600\text{ mg L}^{-1}$ $600\text{ mg L}^{-1}$	540 min	48%	[46]
$\text{TiO}_2$ -coated EP	100 mg	UV light	phenol $0.01\text{ mg mL}^{-1}$	60 min	$21.17\text{ (10}^{-3}\text{ min}^{-1}\text{)}$	[47]
macro/mesoporous anatase $\text{TiO}_2$ ceramic	eighty pieces (20 mg each piece)	UV light	$\text{RhB } 10\text{ mg mL}^{-1}$	180 min	99.4%	[48]
$\text{B}_{0.21}\text{-N-}\text{TiO}_2$ /EP	0.1 g	100 W Hg lamp	$\text{RhB } 10\text{ mg L}^{-1}$	60 min	99.8%	[49]

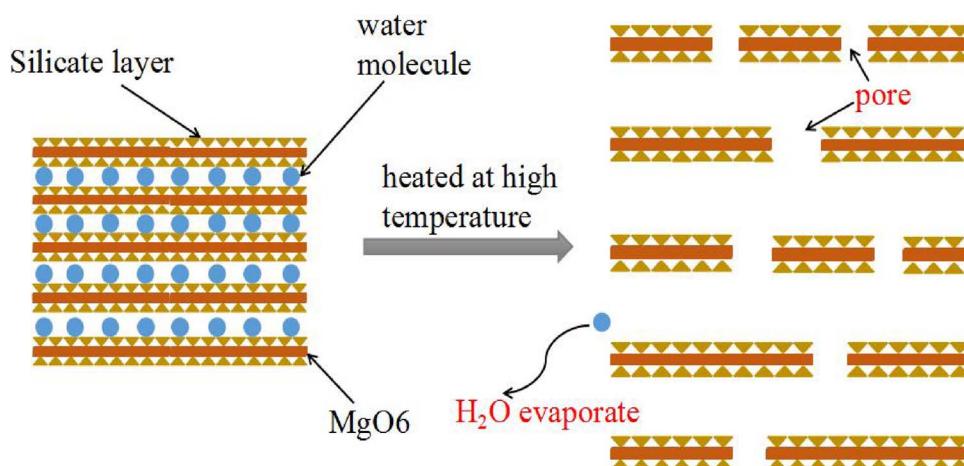


Fig. 6. The proposed mechanism of vermiculite expansion.

such as Mg<sup>2+</sup> and Fe<sup>2+</sup> can replace the position of Al<sup>3+</sup> in the octahedral and Al<sup>3+</sup> can replace the position of Si<sup>4+</sup> in the tetrahedral [60]. Taeyoon et al. [61] made the floating adsorbents with exfoliated vermiculite to remove phosphate in aqueous solution. In this case, the modified vermiculite was prepared with exfoliated vermiculite and glycerol in the ratio of 1/4. This modified vermiculite with highly porous structure showed a good performance of floating adsorbent for the removal of phosphate [62].

When the vermiculite was used as catalyst, there were some modification methods to enhance the catalytic capacity such as acid-activation [63], intercalation with metal oxide pillars including Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and so on, immobilizing nanoparticles of metal oxide onto the silica nanolayers of exfoliated vermiculite [64]. In the past few years, supported photocatalyst had attracted more and more attention because of the advantages and the practical significance of researches. Hence, the preparation of supported photocatalyst immobilizing metal oxide nanoparticles onto expanded vermiculite is an effective method to use solar energy and improve oxidation capacity.

TiO<sub>2</sub> is one of the best known photocatalyst on account of nontoxic, high photoactive, low cost [65] and can support on various substrates [66]. And it has a relatively wide band gap to better absorb photons under the irradiated UV light. Then electrons of TiO<sub>2</sub> will be excited from the valence band to the conduction band to form electron-hole pairs [67]. These electrons and holes can participate in the redox reaction to degrade pollutants. But with the rapidly development of industry and agriculture, some new types of organic/inorganic contaminants such as crude oil were produced. As a result, the degradation effect is disappointed. Because the density of TiO<sub>2</sub> is much larger than water, the TiO<sub>2</sub> will sink when it is put into water [68]. Therefore, TiO<sub>2</sub> is hard to degrade contaminants that are floating on the surface of the water. The floating TiO<sub>2</sub> is very essential and has great development prospect.

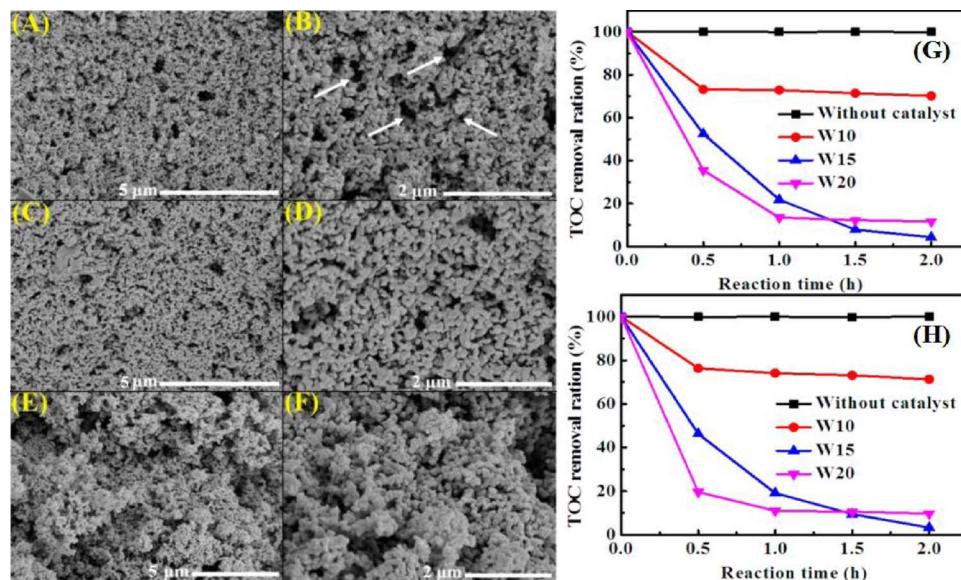
Many scholars and researchers have made a lot of efforts to research the methods of floating photocatalyst which were efficient and environmentally friendly. For example, Xing et al. [69] explored a method to prepare a hierarchical porous TiO<sub>2</sub> ceramic floating photocatalyst in Fig. 7, with ethanediamine-modified Degussa P25 as precursor and through a camphene-based freeze-casting process, subsequently, calcined at high temperature. It could be observed that the TiO<sub>2</sub> ceramic struts were densified with the TiO<sub>2</sub> solid content increasing. Furthermore, many fine pores found in Fig. 7A–B gradually disappeared in Fig. 7C–F with an increase in the TiO<sub>2</sub> solid content. In Fig. 7G, it showed the relationship between the TiO<sub>2</sub> solid content and photocatalytic performance. In brief, 15 wt% TiO<sub>2</sub> solid content (W15) exhibited the highest atrazine TOC degradation rate (95.7%) after 2 h. For W20, the more TiO<sub>2</sub> caused the floating capability of porous TiO<sub>2</sub> ceramic to decline after 1 h. When the TiO<sub>2</sub> solid content was at 10 wt

%, the atrazine TOC degradation rate remained almost unchanged after 0.5 h illumination because the TiO<sub>2</sub> ceramic began to easily disintegrate in water. Therefore, 15 wt% TiO<sub>2</sub> solid content was the optimal condition to achieve high porosity, high mechanical strength, and high photocatalytic activity for the floating porous TiO<sub>2</sub> ceramic. For further verification, thiobencarb degradation experiments were carried out in Fig. 7H, and the results were consistent with that of atrazine. It revealed that the TiO<sub>2</sub> floating photocatalysts had good photocatalytic performance.

In this paper, a new type of floating catalyst through immobilizing TiO<sub>2</sub> nanoparticles onto the silica nanolayers of expanded vermiculite (EV) to form floating TiO<sub>2</sub>/EV photocatalyst is discussed (Table 2). Because EV has extensively microporous structure and high specific surface area, more TiO<sub>2</sub> can coat on the EV which acts as a floating substrate. Hence, the photocatalytic properties of composites are enhanced. However, TiO<sub>2</sub> particles have the potential of separation from the substrate surface because of collisions and hydrodynamic turbulence [69]. In order to better fix TiO<sub>2</sub> on vermiculite, some ways were reported such as low temperature ultrasonic treatment, electrospinning technique and sol-gel method. For instance, Tang et al. [70] synthesized TiO<sub>2</sub>-vermiculite composite nanofibers with the mesh structures by sol-gel approach and electrospinning technique, and the diameter of this composite nanofiber was about 300 nm. Results implied that the TiO<sub>2</sub>-vermiculite composite nanofibers enhanced the absorption properties and degradation of methylene blue [71]. Moreover, the microporous structure and excellent permeability of vermiculite were good for the transfer and diffusion of pollutants [32]. And the TiO<sub>2</sub> could interact thoroughly with pollutants in vermiculite so that the efficiency of floating TiO<sub>2</sub>/EV photocatalyst was high. Importantly, the TiO<sub>2</sub> coating on vermiculite could absorb more energy from sunlight to degrade contaminants because it floated on the surface of water. Therefore, the floating TiO<sub>2</sub>/EV photocatalyst could improve the utilization ratio of solar energy efficiently.



On the whole, due to the optimization of light utilization, the photocatalytic oxidation can achieve the best effect. Furthermore, because of the optimization of light utilization and the maximization of photocatalytic oxidation, more radicals can be produced for the floating TiO<sub>2</sub>/EV photocatalyst to degrade organic pollutants, as showed in Eqs. (1)–(4) [72].



**Fig. 7.** SEM images of the calcined samples at 800 °C from (A, B) 10 wt%, (C, D) 15 wt%, and (E, F) 20 wt %  $\text{TiO}_2$  solid content slurries. And the effect of  $\text{TiO}_2$  solid content on the photocatalytic degradation of atrazine (G) and thiobencarb (H) within 2 h irradiation. Reprinted with permission from Ref. [69].

### 2.3. Glass microbead substrate

Glass microbead, as a type of floating substance, has tiny size, spherical, lightweight, adiabatic, sound insulation, high temperature resistance, abrasion resistance and other multi-functional characteristics. The hollow structure of glass microbeads can greatly reduce the density of composite material. There are two types of hollow glass microbeads: artificial glass microbead and natural glass microbead. Natural glass microbeads are collected from fly ash (FA) by coal-fired power plants which produce electricity. The mainly chemical compositions of FA are  $\text{SiO}_2$ ,  $\text{CaO}$ , and  $\text{Al}_2\text{O}_3$ . The compositions of glass microbeads are different depending on geography, manufacturers, and fuel source. Hollow glass microbead with low cost is a kind of cheap and fine inorganic material, because it is extracted from the FA as by-products. FA represents a mixture of unburned carbon and metal oxides. Among these metal oxides,  $\text{Fe}_2\text{O}_3$  and  $\text{MnO}$  can act as in-situ Fenton-systems [73], which is a good and low cost adsorbent for removing contaminants [74,75].

Glass microbead as a carrier has been widely applied to the floating type catalyst. The recent reports had been summarized in Table 3. Zhao et al. reported floating nitrogen-doped  $\text{TiO}_2$  and Fe-N-codoped  $\text{TiO}_2$  catalyst by sol-gel method in the layers on FA [76]. Studies showed that nitrogen coating could narrow band gap of  $\text{TiO}_2$ . In addition, by surface modification of  $\text{TiO}_2$  with transition metal cations such as  $\text{Fe}^{3+}$  also could extend the photoresponse to visible light region. However, Fe-N-codoped  $\text{TiO}_2$  was always granular or powder material, they were trend to sink into solutions that reduced the catalytic efficiency. More importantly, the application of the catalyst is curbed, because it is difficult to recycle and separate efficiently. In a variety of floating type materials, FA, which is aluminosilicate-rich by-products generated in coal-firing powder plants, has been widely used as a carrier [77–79]. For example, floating Fe-N-codoped  $\text{TiO}_2$  support on FA was favorable for photocatalysis and recycle.

Kim et al. reported the floating type  $\text{TiO}_2$ -coated Pyrex hollow glass beads, which exhibited excellent photocatalytic performance for degradation of algae, *Anabaena*, *Microcystis* and *Melosira* [80,81]. After being irradiated with UV-light in the presence of the  $\text{TiO}_2$ -coated Pyrex glass microbeads, *Anabaena* and *Microcystis*, known as typical cyanobacteria, lost their photosynthetic activity, and the string of *Anabaena* cells and the colonies of *Microcystic* cells were completely separated into individual spherical one. The catalyst could successfully be applied at the eutrophicated wave under sunlight. About 50% of the chlorophyll-a concentration could be resolved by the action of  $\text{TiO}_2$  photocatalysis. Okamoto et al. [82] reported low energy consumption, easy and harmless water cleanup method for preparing self-flotation of fatty acid-coated hollow glass microbeads. The self-flotation of fatty acid-coated hollow glass microbeads played an effective role in water purification.

As a lightweight support, glass microbeads with hollow structure, environmental friendly, low-cost and non-toxic characteristics are indeed excellent carriers to fabricate floating  $\text{TiO}_2$ -based photocatalyst for environmental applications in future.

### 2.4. Cork substrate

Cork is a natural organic polymer material, which is one of the good choices as host materials of inorganic particles, because the excellent electrical, magnetic and optical properties of inorganic materials can be preserved in the polymer matrix. Meanwhile, superhydrophobicity, self-cleaning, antibacterial activity and photodegradation of organic pollutant are the functions of cork products.

The recent studies for floating  $\text{TiO}_2$ -based photocatalyst with cork substrate had been summarized in Table 4. Gao et al. established a robust, anti-acid, and high-temperature humidity-resistant superhydrophobic surface of cork based on a modified  $\text{TiO}_2$  film by fluoralkyl silane [83]. In order to improve the repellency to water, it was a

**Table 2**

Summary of floating  $\text{TiO}_2$ -based photocatalyst with vermiculite substrate.

Name	Weight	Light source	Target & concentration	Time	Removal efficiency	Refs.
exfoliated vermiculite hierarchical porous $\text{TiO}_2$ ceramic	2 g eighty pieces (0.02 g each piece)	sunlight UV light	phosphate Atrazine and thiobencarb 5 mg L <sup>-1</sup>	25 h 2 h	50% 95.7% and 96.7%, respectively	[61] [69]
$\text{TiO}_2$ -vermiculite composite nanofibers	2 wt.% of vermiculite	500 W high-pressure mercury lamp	MB 10 mg L <sup>-1</sup>	100 min	100%	[70]

**Table 3**Summary of floating  $\text{TiO}_2$ -based photocatalyst with glass microbead substrate.

Name	Weight	Light source	Target & concentration	Time	Removal efficiency	Refs.
Fe-N-codoped $\text{TiO}_2$ /fly ash cenospheres	0.2 g	visible light	$\text{RhB mg L}^{-1}$	4 h	89%	[76]
hollow $\text{TiO}_2$ /fly ash cenospheres	1.5 g	sunlight	$\text{MB 30 mg L}^{-1}$	9 h	0.0922 ( $\text{min}^{-1}$ )	[80]
Fe-N-codoped $\text{TiO}_2$ /fly ash cenospheres	–	sunlight	<i>Microcystis Melosira</i>	60 min	50%	[81]

**Table 4**Summary of floating  $\text{TiO}_2$ -based photocatalyst with cork substrate.

Catalyst	weight	Condition	Target/Concentration	Removal efficiency	Refs.
$\text{TiO}_2$ /cork	–	UV light	water	self-clean	[83]
Ag- $\text{TiO}_2$ /cork	–	UV light	phenol 67.2 $\text{mg L}^{-1}$	80%	[84]
$\text{TiO}_2$ /cork	–	UV light	color of sample	color was lost	[85]
$\text{TiO}_2$ /cork	–	UV light	congo red 10 $\text{mg L}^{-1}$	85%	[86]

crucial role that decorated trimethoxysilane on  $\text{TiO}_2$ -based cork surface. The water contact angle was larger than 150° when the  $\text{TiO}_2$ /cork was immersed in 0.1 M hydrochloric acid solution for one week, boiled at 150 °C for 10 h, or irradiated for 24 h under UV light. Multi-functions including anti-acid, super repellency toward to water, and high-temperature-humidity-resistant were shown on the prepared cork surface. According to the results, the functional coating on the cork surface provided an efficacious field of the cork works. Gao et al. had also established a robust superhydrophobic antibacterial by Ag- $\text{TiO}_2$  composite film coat on cork structure for photodegradation of phenol under visible-light illumination [84]. It is a novel floating  $\text{TiO}_2$ -based photocatalyst with excellent photocatalytic activity, leading to an important application of self-cleaning.

Pori et al. had prepared that the structure of  $\text{TiO}_2$ /cork coatings, using hydrothermal deposition of rutile particles from  $\text{TiCl}_4$  aqueous solutions [85]. Using hydrothermal method in  $\text{TiCl}_4/\text{HCl}$  aqueous solutions at 750 °C and developed for the deposition of rutile  $\text{TiO}_2$  particles on a cork surface. The thickness of the particles deposited on the wood surface, cell wall, and lumen surface depended on the amount of  $\text{TiCl}_4$  added. Sboui et al. reported a new floating salicylic acid (SA) modified  $\text{TiO}_2$  photocatalyst with a palm trunk (PT) as supports [86]. PT as a nature material has characteristics of easy access, cheap and nontoxic. The prepared photocatalyst under sunlight irradiation could degrade organic contaminants in water such as dyes, phenols, and the photocatalyst could be reused four times before losing high activity. Results showed that PT could be used to support  $\text{TiO}_2$ -SA, and then the floating photocatalyst could be prepared. Cork as base of floating materials composite with  $\text{TiO}_2$  could improve the efficiency of photocatalytic performance.

Cork has very good flexibility, sealing, heat insulation, sound insulation, electrical insulation, friction resistance, non-toxic, tasteless and so on, resulting in excellent floating substances. In summary, cork is widely used in the field of floating photocatalysis due to its unique characteristics, especially composited with  $\text{TiO}_2$ , which shows excellent photocatalytic activity for organic pollutants. At the same time, the future research is attracted to overcome the defect in physics due to the fact that the main shortcomings of existence are poor physical properties.

## 2.5. Graphite substrate

Graphite with good conductivity, permeability, superconductivity, hydrogen storage and adsorption properties can form the different 3D layer structure. Graphene is composed of carbon atoms in  $\text{sp}^2$  hybridization way and then form the thin film of the honeycomb. It is a

**Table 5**Summary of floating  $\text{TiO}_2$ -based photocatalyst with graphene substrate.

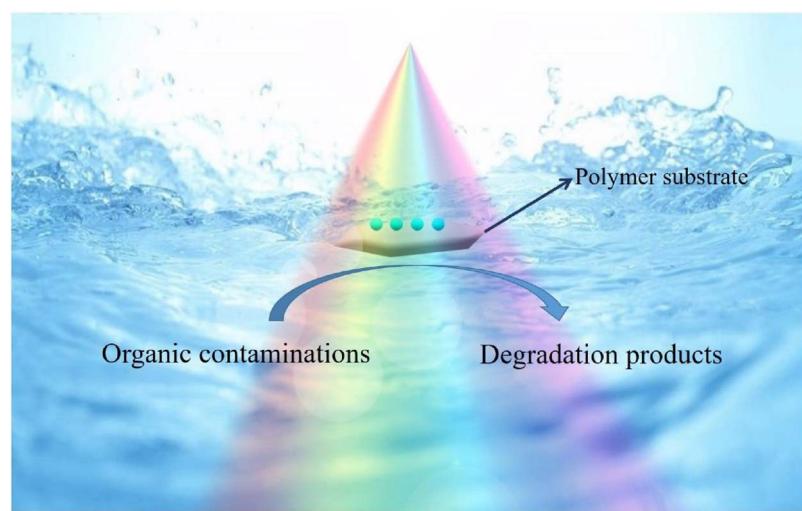
Catalyst	weight	Condition	Target/Concentration	Removal efficiency	Refs.
$\text{TiO}_2$ -graphene	0.1 g	UV light	phenol 10 $\text{mg L}^{-1}$	81%	[87]
EG- $\text{TiO}_2/\text{ZnO}$	0.3 g	UV light	$\text{CO}_2$ 0.3 $\text{L min}^{-1}$	51%	[88]
$\text{TiO}_2$ -graphene	60 mg	UV light	recover the copper (9.62 $\text{cm}^2$ cross-section area)	99.4%	[89]
$\text{TiO}_2$ -graphene	0.2 g	UV light	RhB 0.02 mM	95%	[90]
$\text{TiO}_2$ -graphene	0.02 g	UV light	diesel 500 $\text{mg L}^{-1}$	88%	[91]

kind of the only one atomic layer thickness of 2D materials, so called single atomic layer of graphite. Further, another material is inserted into the interlayer between the layers of graphite, the novel materials with excellent performance can be successfully fabricated. Due to its special structure, it is a kind of the excellent float lightweight catalyst carrier.

The recent studies of floating  $\text{TiO}_2$ -based photocatalyst with graphite substrate are summarized in Table 5. Jiang et al. established that the photocatalytic activity of  $\text{TiO}_2$ -graphene had been enhanced by in-situ growth of  $\text{TiO}_2$  in interlayers of expanded graphite (EG). [87]. Especially,  $\text{TiO}_2$ -graphene composite synthesizing by subsequent thermal treatment at high temperature under nitrogen showed higher photocatalytic degradation rate of phenol under visible light and UV when compared with Degussa P25. Expanded graphite increased charge separation that was beneficial to the enhanced photocatalytic performance, improved light absorbance and high absorptivity for pollutants.  $\text{TiO}_2$ -graphene also had good functionality for removing copper and degrading Rh B, and diesel. Ramanathan et al. synthesized a fresh floating catalyst by acid-catalyzed and sol-gel two-step methods [89]. This kind of the catalyst was modified by organic silicate, which could be considered as a binder between catalyst and exfoliated graphite. The purpose of this study was to recover the copper from aqueous solutions. The results showed that the floating catalyst could be used to prolong the duration, showed good regeneration capability and it could peel off amount of the recovered copper. Modestov et al. also discovered this kind catalysts, it was optimized for the degradation of RhB [90]. The photodegradation efficiency of the coated photocatalyst film was between 50 and 95%. Zhang et al. established that based on loading Bi/N-doped  $\text{TiO}_2$  on expanded graphite C/C (EGC) using a novel sol-gel method to graft two materials, in order to degrade diesel under visible light [91]. All N- $\text{TiO}_2$  composites modifying Bi had much better photocatalytic activity for the diesel degradation than that of N- $\text{TiO}_2$  under visible light irradiation.  $\text{TiO}_2$  was evenly distributed on the composite when calcined at 550 °C, which showed the highest photocatalytic activity.

Shahna et al. prepared photocatalyst using non-thermal plasma (NTP) combined with EG- $\text{TiO}_2/\text{ZnO}$  to degrade Chlorobenzene [88]. Both the removal efficiency and the  $\text{CO}_2$  selectivity were enhanced respectively. The byproducts, which output from the combine system, were decreased dramatically. Rising the applied voltage and residence time led to an increase in the  $\text{CO}_2$  selectivity and removal efficiency. On the whole, the combined system was preferred because of the lower harmful byproducts.

Graphite, especially expanded graphite, is indeed excellent substrate for fabricating floating photocatalyst due to the special



**Fig. 8.** Schematic depiction of the floating optimized photocatalyst of  $\text{TiO}_2$  coated on polymer.

structures. The special 2 D layered structure will offer good hosts to prepare other floating semiconductor photocatalyst.

#### 2.6. Polymer substrate

The use of organic polymer-based (such as polypropylene, polystyrene, etc.) photocatalyst to degrade contaminants in the wastewater has attracted the attention of many researchers because the organic polymer has the following advantages: (1) The organic polymer-based photocatalyst has a high durability and can be used for a long time under different conditions. (2) Organic polymer is easy obtained and cheap. (3) Organic polymers are generally hydrophobic so that organic contaminants are adsorbed on the surface, which improve photocatalytic performance. (4) Organic polymer is generally low melting point, has good thermoplastic, and can be made into a variety of shapes which can fully be combined with the catalysts. (5) Organic polymer density is generally low. As showed in Fig. 8, organic contaminants are degraded by floating polymer-based photocatalyst under solar light irradiation.

The recent studies for floating photocatalyst with polymer substrate are summarized in Table 6. Polypropylene (PP) is a commonly substrate of floating photocatalyst. The PP substrates have the advantages of low price, reasonably good mechanical strength, high UV-resistance, chemical stability, and excellent processing flexibility in the final shape and dimension of the products. Han et al. used a low temperature hydrothermal method to prepare floating photocatalyst supported on PP

granules [92]. To increase the visible light photocatalytic active, nitrogen was doped into  $\text{TiO}_2$  by adding trimethylamine (TEA). Because of the low melting point of PP, the method of low temperature hydrothermal was adopted to prepare the floating photocatalyst.  $\text{TiO}_2$  was prepared by sol-gel method using titanium *n*-butoxide as precursor, acetyl acetone or acetic acid as inhibitor. The light absorption edge of floating photocatalyst was extended to 800 nm. The photocatalytic activity of prepared floating photocatalyst was evaluated by decolorization of methyl orange dye under both UV and the visible light. The photocatalytic experiments showed that  $\text{TiO}_2$  with the treatment of TEA photocatalyst probably had lower band gap energy and enhanced photocatalytic activity. Additionally, the photocatalyst could float on the surface of water and fully utilize sunlight to degrade organic pollutants in wastewater.

Tu et al. reported that the floating composite photocatalyst with two-layered configuration was synthesized by immobilizing powdered activated carbon and  $\text{TiO}_2$  nanoparticles on the PP granules [93]. Powdered activated carbon layer was immobilized onto PP granules surface according to the thermal bonding, and then the  $\text{TiO}_2$  nanoparticles layer was loaded on the powdered activated carbon through suspension deposition. Comparing with the powdered photocatalyst, the double-layer structure had certain advantages. The floating photocatalyst showed good photocatalytic stability because powdered activated carbon not only acted as a middle layer, but also prevented the degradation of organic polymer substrates during the photocatalytic reaction. This double-layer floating photocatalyst enhanced the

**Table 6**  
Summary of floating  $\text{TiO}_2$ -based photocatalyst with polymer substrate.

Catalyst	weight	Light source	Target & concentration	Time	Removal efficiency	Refs.
$\text{TiO}_2$ /polypropylene	15–20 mg	UV-vis light	$\text{MO } 15 \text{ mg L}^{-1}$	4 h	about 65%	[92]
$\text{TiO}_2$ /polypropylene granule	138 mg	UV light	phenol $20 \text{ mg L}^{-1}$	8 h	100%	[93]
$\text{TiO}_2$ /polypropylene fabric	a piece ( $d = 47 \text{ mm}$ )	UV-vis light	$\text{MO } 15 \text{ mg L}^{-1}$	240 min	100%	[94]
$\text{TiO}_2$ /polypropylene	a piece	UV-vis light	$\text{MO } 15 \text{ mg L}^{-1}$	120 min	about 65%	[95]
iron oxide/cloth canvas	–	UV light	$\text{RhB } 5 \text{ mg L}^{-1}$	90 min	93.2%	[96]
$\text{TiO}_2$ /expanded polystyrene	1.0 g	solar light	drimaren red, indigo carmine, and $\text{MB } 50 \text{ mg L}^{-1}$	240 min	almost 100%	[97]
$\text{Ag}^+$ -doped $\text{TiO}_2$ /polystyrene	0.05 g	UV and solar light	$\text{MB } 5 \text{ mg L}^{-1}$	5 h	94% (UV) and 83% (solar light)	[98]
$\text{TiO}_2$ /polyurethane foam	forty pieces	sunlight	$\text{RhB} + \text{Cr}^{\text{VI}}, \text{MO} + \text{Cr}^{\text{VI}}$ and $\text{MB} + \text{Cr}^{\text{VI}} 10 \text{ mg L}^{-1}$	150 min	above 90%	[32]
$\text{Ag}/\text{TiO}_2$ /graphene/polyurethane foams	0.3 g	visible light	diesel $15 \text{ g L}^{-1}$	16 h	76%	[100]
$\text{TiO}_2$ /low density polyethylene	1 g	UV and solar light	$\text{MB } 0.16 \text{ mmol L}^{-1}$	240 min	35% (UV) and 30% (solar).	[101]
$\text{C}_3\text{N}-\text{TiO}_2$ /polytetrafluoroethylene	$1 \text{ g L}^{-1}$	visible light	$\text{MO } 20 \text{ mg L}^{-1}$	4 h	96.9%	[102]
$\text{TiO}_2$ /poly (methyl methacrylate)	a thin film	sun-light	4-NP $0.144 \text{ mM}$	400 min	above 80%	[103]

removal efficiency of phenol due to its two-layer structure and the synergistic effect between activated carbon and  $\text{TiO}_2$ . Although PP particles improved the efficiency of light utilization, the loading rate of  $\text{TiO}_2$  particles on the surface of PP particles was lower than that of PP fabric. Then, Han et al. prepared a high performance floating photocatalyst, which had novel structures with different crystalline  $\text{TiO}_2$  layers loaded on the PP fabric surface [94]. To increase the loading rate of  $\text{TiO}_2$ , the flower-like rutile  $\text{TiO}_2$  was first supported on the PP fabric surface and the anatase  $\text{TiO}_2$  was immobilized on the rutile  $\text{TiO}_2$  layer to form a double-layer structure. The density of all prepared photocatalyst was less than the density of water so that the photocatalyst could float on the water. The photocatalytic property of the prepared photocatalyst was demonstrated by photocatalytic degradation of methyl orange (MO) under UV and visible light irradiation, and the results proved that it had excellent photocatalytic performance. Han et al. [95] further studied the effect of the thickness of the  $\text{TiO}_2$  floating composite photocatalyst film based on PP fabric under different light conditions. Photodegradation experiments were based on MO dyes that served as the target model. The experimental results showed that the photocatalytic activity of the photocatalyst, under UV irradiation, was not changed with the increase of the catalyst thickness, but it was enhanced under visible light irradiation. Oliveira et al. prepared a novel floating iron oxide photocatalyst device in a very simple impregnated way based on PP non-woven fabric canvas [96]. The photodegradation activity of the floating photocatalyst was evaluated by photodegradation of RhB under UV irradiation, which had high photocatalytic activity after five times of reuse. The photocatalyst using non-woven fabric canvas as substrate could be used to treat wastewater under the non-mechanical stir and solar illumination.

Polystyrene is a hydrophobic material and can pre-concentrate organics from water on its surface to improve the removal and oxidation efficiency, thereby increasing the efficiency of adsorption and subsequent oxidation of the contaminants. Magalhães et al. reported the floating photocatalyst that could effectively utilize the sunlight to degrade dyes, which were prepared by grafting commercial  $\text{TiO}_2$  (P25) onto the surface of expanded polystyrene beads [97]. This floating photocatalyst had the advantages such as simple preparation process, high performance, high stability and low cost. Experiments showed that the floating photocatalyst had high photocatalytic performance after repeated use for 4 times. Singh et al. used two different solvent-cast methods to prepare two kinds of photocatalyst with high stability, effectiveness and floatability [98]. The photocatalyst of silver ion-doped  $\text{TiO}_2$  was fixed onto or into the polystyrene substrate. One was impregnated  $\text{TiO}_2$  photocatalyst and the other was strewn  $\text{TiO}_2$  photocatalyst, as showed in Fig. 9. The photodegradation experiment, which aimed at degrading methylene blue (MB) dyes in aqueous solutions at natural pH under both UV and sunlight irradiation, demonstrated that this novel floating photocatalyst was highly efficient and recyclable.

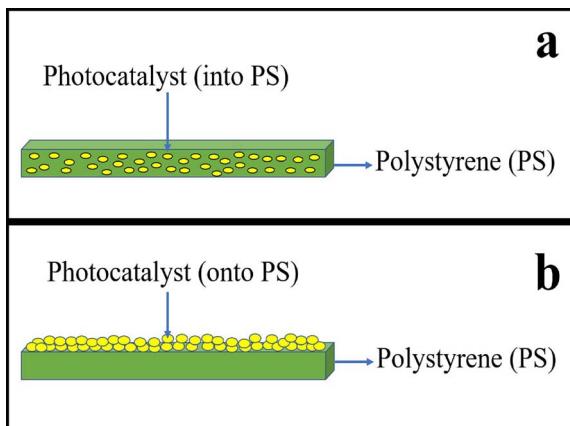


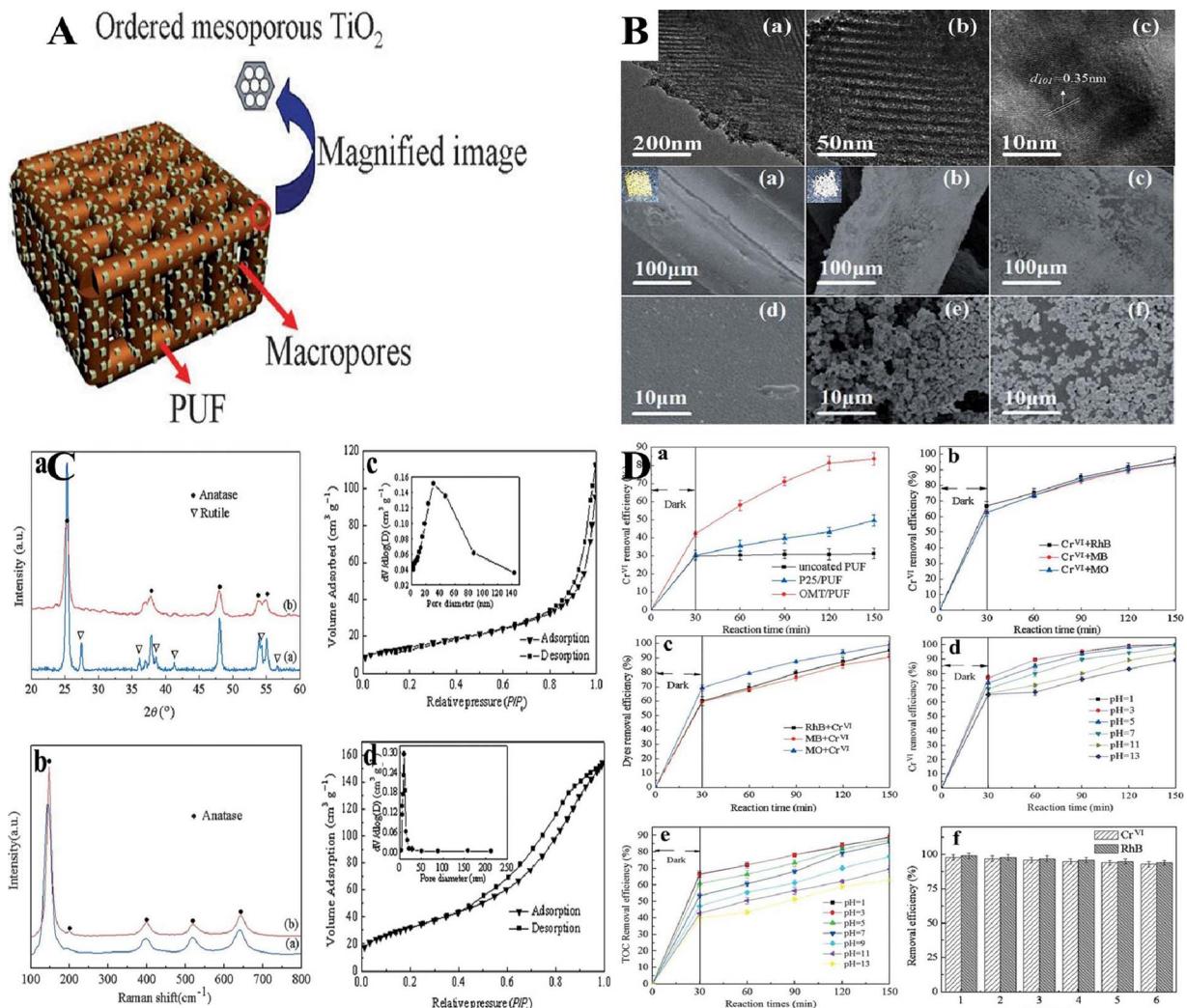
Fig. 9. Schematic view of impregnated (a) and strewn (b) to doped  $\text{TiO}_2$  photocatalysts.

The optimum photocatalytic activity of impregnated photocatalyst and strewn photocatalyst was up to 86 and 94% respectively, under UV irradiation. While under the sunlight, the optimum photocatalytic activity of impregnated photocatalyst and strewn photocatalyst was up to 68 and 83%, respectively.

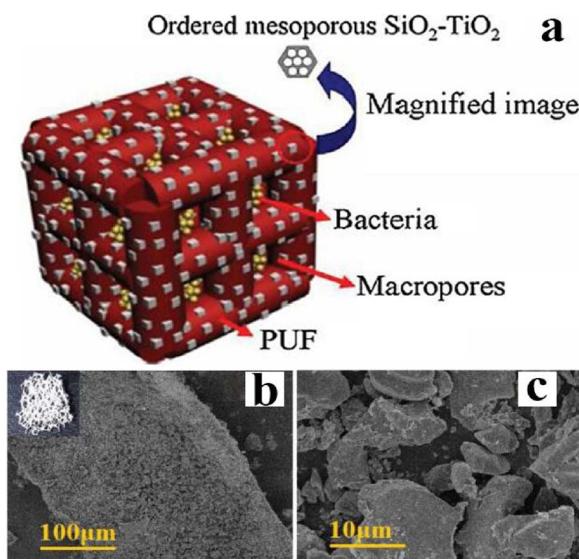
Polyurethane foam (PUF) as a commonly used polymer, it has a high specific area, surface roughness, strength, porosity, and durability, and it is a light-weight material which can act as substrate. Zhang et al. successfully prepared a multi-functional ordered mesoporous  $\text{TiO}_2$  (OMT)/PUF foam floating photocatalyst by low temperature ultrasonic and deposition methods [32]. Schematic view of the photocatalyst is showed in Fig. 10A. TEM images showed the morphology of ordered mesoporous  $\text{TiO}_2$  and SEM image of the floating photocatalyst indicated that the PUF surface was coated by OMT particles, as showed in Fig. 10B. The OMT was anatase and its pore-size reached 12 nm as showed in Fig. 10C. The photocatalyst had a variety of the functions including adsorption and degradation of pollutants, and removal of heavy metal ions in water. The performance of the photocatalyst had been demonstrated by degrading organic dyes and simultaneously removed hexavalent chromium ions as showed in Fig. 10D. The results showed that the heavy metal ions in the mixed solution could be completely removed under sunlight irradiation for 2 h, and the degradation rate of the dye was also more than 90%. The photocatalyst could be reused six times without significant changes. This novel floating OMT/PUF foam will have potential applications in environmental field. Furthermore, Zhang et al. prepared a high thermostable ordered mesoporous  $\text{SiO}_2$ – $\text{TiO}_2$ /PUF floating photocatalyst [99], as shown in Fig. 11. This photocatalyst had been used in a photocatalytic circulating-bed biofilm reactor and the reactor exhibited excellent degradation properties.

Ni et al. prepared a novel floating photocatalyst based on polyurethane composite foams [100]. This novel floating photocatalyst was composited with silver,  $\text{TiO}_2$  and graphene. The photocatalytic activity of prepared floating photocatalyst was examined by photodegradation of diesel under UV and visible light irradiation. Under visible light irradiation, the diesel photodegradation capacity was 76%, and the diesel photodegradation capacity was enriched with increasing solution temperature from 5 to 30 °C, and the optimum pH was from 7.5 to 8.0. The density of prepared photocatalyst was in the range of 0.17–0.31 g  $\text{cm}^{-3}$ , which was much lower than that of water because a lot of holes had been created during the prepared procession. These holes ensured the floating properties of the photocatalyst. Due to the good stability, it could be repeated for 5 times while the degradation rate showed no significant change. Magalhaes et al. prepared novel floating  $\text{TiO}_2$ /low density polyethylene (LDPE) photocatalyst using different  $\text{TiO}_2$  contents (32, 68, and 82 wt.%) through a suspension of  $\text{TiO}_2$  (Degussa P25) in LDPE dissolved in xylene at 80 °C [101]. The photocatalytic activity was demonstrated by the degradation of methylene blue as a probe molecule under UV (254 nm) and sunlight irradiation. The prepared photocatalyst exhibit higher photocatalytic activity in discoloration and TOC removal compared to pure  $\text{TiO}_2$ . The density of the photocatalyst was in the range of 0.1–0.5 g  $\text{cm}^{-3}$ , and holes were generated during the preparation of the photocatalyst, so that the photocatalyst had buoyancy that could float on the water surface in contact with air to make full use of light. Recovery of photocatalyst through simple screening, experiments had shown that photocatalyst could be reused at least 8 times. The results showed that the degradation effect of the previous three dyes was similar. Thereafter, the degradation effect for the next five degradation reactions was in the range of 93–97%. These results clearly indicated that the floating photocatalyst could be reused at least for several times without any significant loss of activity.

In addition to the above polymers, other polymers have also been explored. Zhong et al. used  $\text{TiO}_2$  nanoparticles and polytetrafluoroethylene to successfully prepare a floating, carbon and nitrogen co-doped  $\text{TiO}_2$ /polytetrafluoroethylene flakes photocatalyst [102]. It was reported that the floating photocatalyst was able to remove organic



**Fig. 10.** Schematic view of the floating macro/mesoporous OMT/PUF photocatalyst (A), TEM and SEM images of the prepared photocatalyst (B), XRD patterns, Raman spectra, and N<sub>2</sub> adsorption isotherms and the corresponding pore size distributions of Degussa P25 and OMT (C), and photocatalytic degradation performance (D). Reprinted with permission from Ref. [32].



**Fig. 11.** Schematic view of the floating macro/mesoporous SiO<sub>2</sub>-TiO<sub>2</sub>/PUF carrier (a), and SEM images of the SiO<sub>2</sub>-TiO<sub>2</sub>/PUF (view on outside) (b and c). Reprinted with permission from Ref. [99].

pollutants in wastewater under various light irradiation. The density of prepared photocatalyst was 0.93 g cm<sup>-3</sup>, which was lower than that of water. The photocatalytic activity was evaluated by photodegradation methylene orange solution under visible light irradiation. And the final photodegradation rate was up to 96%. Large surface area and small TiO<sub>2</sub> particle size led to the improvement of photocatalytic activity and adsorption performance. After three times recycling, the photocatalytic efficiency of the photocatalyst was still up to 67%, indicating the high stability. It was showed that the prepared photocatalytic material was able to restore and protect environment due to its economic factors, thermal stability, and highly photogradation activity. Floating photocatalyst can not only be used to degrade pollutants in water, but also can be used to kill microorganisms in water. Salabat et al. [103] explored a new type reducing photocatalyst that was made up of TiO<sub>2</sub> and poly (methylmethacrylate), on the basis of micromulsion technology. The reducing photocatalyst was applied to the disinfection of microorganism in wastewater and the photocatalytic degradation of pollutants.

Despite the advantages of organic polymer substrates, there are still some obstacles to overcome. For example, the organic polymer substrate is photodegraded by catalyst. At the same time, the additional pollutant is generated and the service life is shortened. Researchers have come up with a number of solutions to overcome the obstacles in practical application.

**Table 7**Summary of floating  $\text{TiO}_2$ -based photocatalyst with another immobilized substrate.

Catalyst	weight	Light source	Target & concentration	Time	Removal efficiency	Refs.
$\text{TiO}_2/\text{LECA}$	$25 \text{ g L}^{-1}$	solar light	ammonia 975 ppm	3 days	96.5%	[104]
$\text{TiO}_2\text{-ZnO/LECA}$	$25 \text{ g L}^{-1}$	UV light	ammonia 50–500 $\text{mg L}^{-1}$	3 h	95.2%	[105]
$\text{TiO}_2/\text{organosilica}$	15–60 mg	solar light	$\text{O}_2$ -saturated solution of 5% aqueous formic acid	60 min	evolved $\text{CO}_2$	[106]
$\text{TiO}_2/\text{autoclaved cellular concrete}$	30 mg	UV light	atrazine 5 $\text{mg L}^{-1}$ , diclofenac 5 $\text{mg L}^{-1}$ and indigo carmine 30 $\text{mg L}^{-1}$	350 min	–	[107]

**Table 8**

Advantage and disadvantage of different immobilized floating photocatalyst.

Substrate	Advantage	Disadvantage
perlite	the relatively large grains millimeter-level	poor mechanical strength short suspension time
vermiculite	non-toxic, expansion and dehydration-hydration	short suspension time
glass microbead	tiny size, adiabatic, sound insulation, high temperature resistance and abrasion resistance	poor electrochemical performance
cork	flexibility, heat insulation, sound insulation and friction resistance	inflammable putrescibility
graphite	good conductivity, permeability and hydrogen storage	difficult preparation difficult recycled
Polymer	high durability, cheap, hydrophobic, generally low density	photodegraded by catalyst low thermal stability

## 2.7. Other immobilized photocatalyst

In addition to the substrates mentioned above, researchers also explore photocatalyst with other materials as substrates, such as light expanded clay aggregate (LECA) substrate [103,104], silicone substrate [105] and autoclaved cellular concrete (AAC) [106].

The recent studies for floating  $\text{TiO}_2$ -based photocatalyst with another immobilized substrate are summarized in Table 7. LECA is a special kind of clay, which is made of particles, and subsequently calcined at very high temperature in rotary kiln. It is a novel, porous substrate with low density at the same time. Shavisi et al. [103] reported a novel floating  $\text{TiO}_2/\text{LECA}$  photocatalyst for ammonia degradation in petrochemical wastewater under solar light. The floating photocatalyst was formed by immobilizing  $\text{TiO}_2$  (P25) on the LECA. The photocatalytic degradation experiments were carried out in two reactors under sunlight, one equipped with aeration device and the other had a stirring device. The experimental results showed that the removal efficiency of ammonia increased with the rise of pH, the best removal efficiency was 96.5% at pH = 11, and the optimum photocatalyst dosage was  $25 \text{ g L}^{-1}$ . Mohammadi et al. [104] successfully synthesized composite  $\text{TiO}_2\text{-ZnO}$  photocatalyst with LECA as supports by a simple and efficient method. The photocatalytic activity of the prepared photocatalyst was examined by photo-oxidation of ammonia under UV irradiation in the photocatalytic reactors. The experimental results showed that the photocatalyst had high activity and the removal rate was 95.2% in a short time. The optimum catalyst dosage was  $25 \text{ g L}^{-1}$ , and the optimum pH was 11 when ammonia-removal rate was up to maximum.

Maki et al. [105] prepared a floating  $\text{TiO}_2$  photocatalyst with an amino group-based silicone particle as a substrate. The photocatalytic activity was demonstrated by photo-oxidation of the acetic acid in  $\text{O}_2$ -saturated water under sunlight irradiation. The experimental results revealed that calcining at  $400^\circ\text{C}$  showed a floating property and good catalytic activity because the higher temperature destroyed the methane groups on the catalyst surface and increased the crystallinity of  $\text{TiO}_2$ . Andrade et al. [106] reported novel  $\text{TiO}_2$  floating photocatalyst with AAC as the substrate to degrade organic pollutants in wastewater. To evaluate the photocatalytic activity of the prepared floating photocatalyst, the photodegradation of indigo carmine in solution was studied under UV irradiation. Three different degradation systems,  $\text{TiO}_2/\text{AAC/UV}$ ,  $\text{TiO}_2\text{-P25/UV}$  and photolysis (UV irradiation), were used in the experiment. The results showed that  $\text{TiO}_2/\text{AAC/UV}$  system had the highest catalytic efficiency (100%) compare with the other two systems under UV irradiation. It was also worth noting that the toxicity of diclofenac and indigo carmine did not change significantly before and

after photocatalytic degradation, but for atrazine, the toxicity was only 50% after degradation. The reason was not possible to assure, but it may be due to the formation of by-product or residual atrazine in solution.

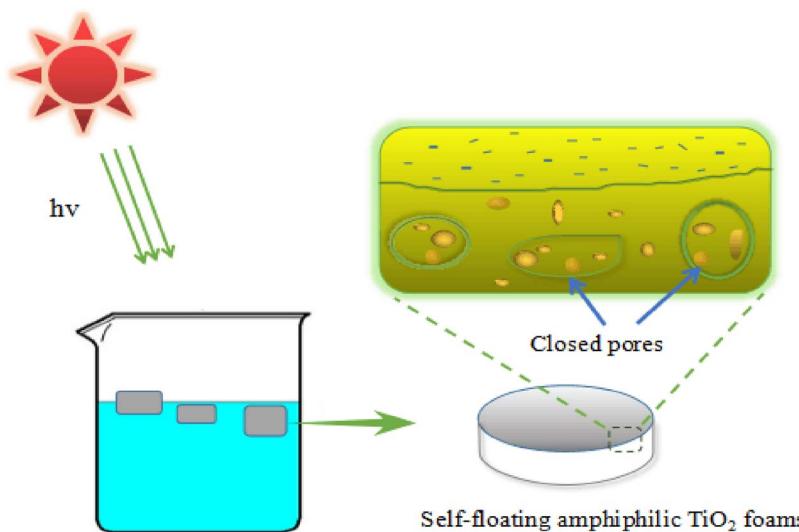
In summary, the immobilized floating photocatalyst have been rapid developed. Due to expend several times, perlite and vermiculite process have large void fraction that is beneficial for the absorption. The synergistic effect can be achieved with photocatalyst. As for cork and glass microbead, it comes from nature and electricity generation respectively, meaning rich content of floating substance. Similarly, the organic polymer-based materials have a high durability and can be used for a long time under different conditions, and the characteristic of easy obtain and cheap further confirm that it can be considered as a carrier of floating photocatalyst. Additionally, Table 8 has been summarized to give the advantages and disadvantages. Although the effectively degradation rate is achieved by those floating based photocatalyst, the amount of  $\text{TiO}_2$  is difficulty confirmed. The Non-immobilized and self-floating photocatalyst is conducive to understanding of floating photocatalyst.

## 3. Non-immobilized floating photocatalyst

Apart from the general immobilized floating photocatalyst discussed above, the non-immobilized floating photocatalyst have been studied as an alternative material to address the global issue of water pollution [108]. Non-immobilized floating photocatalyst gains merits from the cost, the utilization of sunlight source and the high property of self-control. On the other hand, without the floatable catalyst supports such as perlite, vermiculite, glass microbead, cork, expanded graphite or polymer, non-immobilized floating photocatalyst have less adverse effects than the former owing to the potential harms of the substances.

Semiconductor  $\text{TiO}_2$  has been widely studied as the photocatalytic material, mainly due to the effective degradation of organic contaminants in aqueous medium. The structure of  $\text{TiO}_2$  can be modified by many different methods so that photocatalyst floats on the surface of wastewater. On account of the similar pores in truss, it is possible to project and fabricate support-free self-floating porous  $\text{TiO}_2$  [109].

Non-immobilized self-floating photocatalyst, as a representative of advanced oxidation processes (AOPs) catalysts [110,111], can degrade the contaminants in-situ but have the same issues (the huge quantity of photocatalyst and the matter of the photocatalyst isolation) with pure  $\text{TiO}_2$  photocatalyst need to be addressed. The self-floating photocatalyst is developed (as shown in Fig. 12), there is no doubt that the application will attract more researchers who commit to protecting the environment.

Fig. 12. Schematic depiction of the self-floating  $\text{TiO}_2$  photocatalyst.

Xia et al. [112] reported the synthesis of large-scale floating  $\text{TiO}_2$  nanorod arrays through a hydrothermal reaction, without any surfactants, in the condition of high temperature and non-surfactants. This one-step synthesis was a new way to the fabrication of floating photocatalyst and free-standing nanorod arrays, which was efficient to the photodecomposition of floating organics such as crude oil and could also be used as photoanodes for flexible dye-sensitized solar cells (DSSCs). As to the free-standing floating photocatalyst, light weight is another profitable element to pursue. Zhang et al. [109] demonstrated a novel self-floating amphiphilic black  $\text{TiO}_2$  foam with 3D macro-mesoporous architecture which could extend photoresponse to visible light region and present an obvious photocatalytic activity to resolve the recycle issues. Besides, the mineralization of some floating organic pollutants and pesticides revealed the high photocatalytic activity. Through freeze-drying method and cast molding technology, the self-floating black  $\text{TiO}_2$  foams with closed pores were fabricated eventually after surface hydrogenation at 600 °C as shown in Fig. 13A, which could float on water and utilize solar-light efficiently.

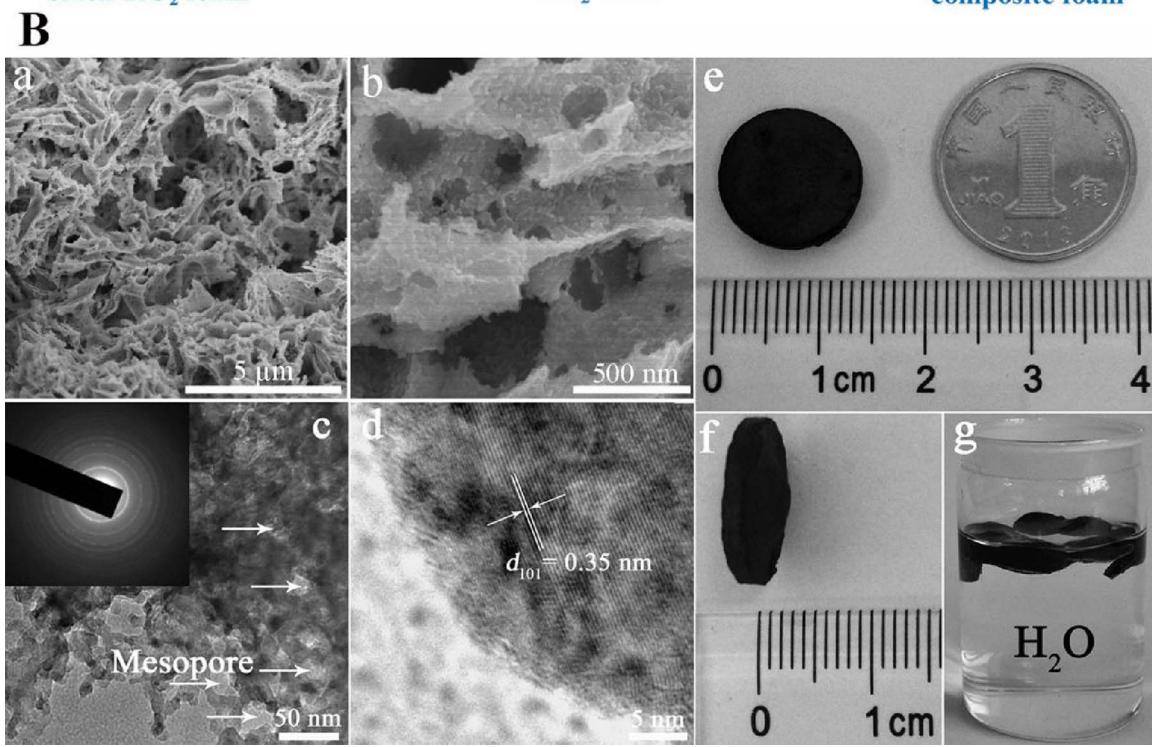
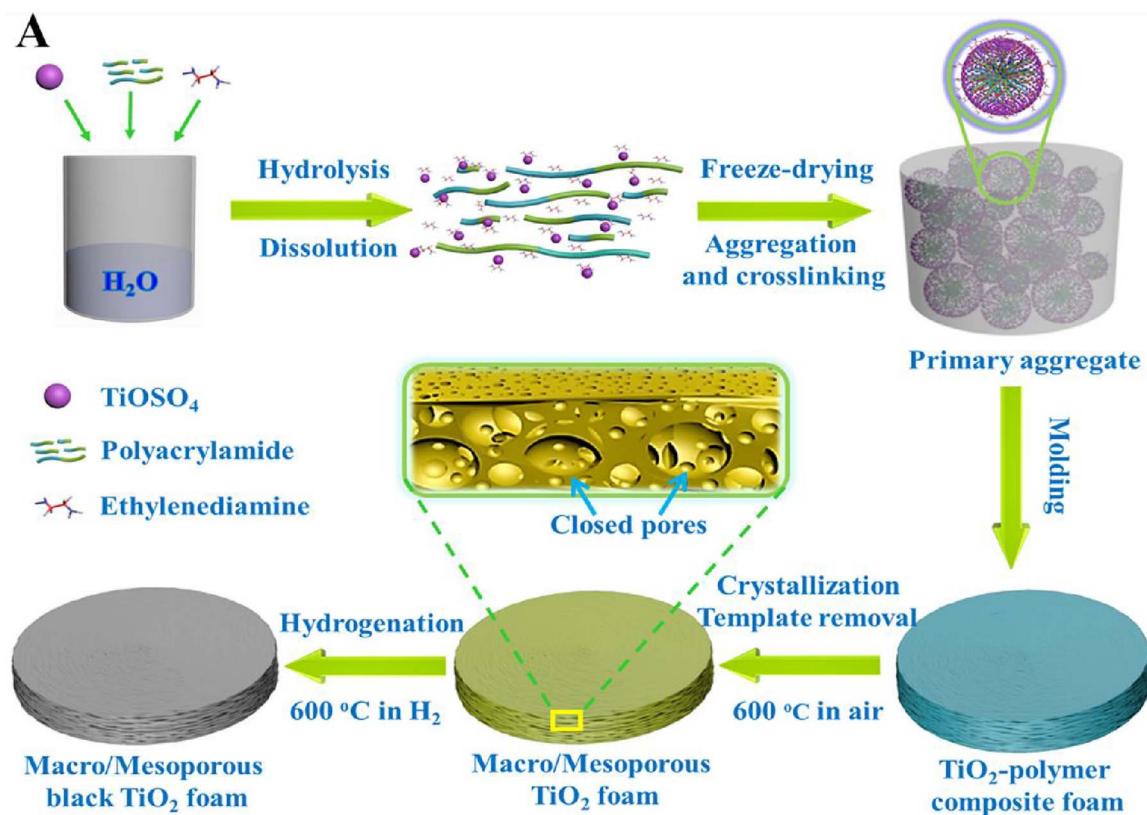
As shown by SEM and TEM (Fig. 13B), the macro-mesopores foam-like structure was slightly changed during the calcination process, and the lattice fringe spacing was estimated to be ~0.35 nm. Besides, the morphologies of black  $\text{TiO}_2$  foams were close to a dime, this kind of photocatalyst could float on the water surface and enhance the illumination directly. Moreover, the transformed amphiphilic 3D macro-mesoporous networks promoted the transportation and adsorption and the floating feature with  $\text{Ti}^{3+}$  benefited light-harvesting, leading to the enhancement of photocatalytic activity. Except for changing the characteristics of  $\text{TiO}_2$  to enhance the photocatalytic activity and increase the visible light response, the approach of doping the semiconductor  $\text{TiO}_2$  with a noble metal (e.g. Ag, Cu, Pt, Au, and Pd) or injecting the  $\text{TiO}_2$  nanoparticles with lipid gains widely attention. Devi et al. [113] investigated silver metallized  $\text{TiO}_2$  particles with enhanced photocatalytic activity to degrade azo dye methyl oranges. The photocatalytic activity of the Ag- $\text{TiO}_2$  system was compared before and after the surface modification, which was increased when silver particles deposited on the P25 surface. The existence of silver mostly enhanced the efficiency of charge separation from electron-hole pairs and strengthened the photocatalytic oxidation of organics that were mainly oxidized by the holes. Furthermore, pH had an effect on the photodegradation rate as well, and the degradation was most efficient at pH 6.6 for Ag- $\text{TiO}_2$ . Meanwhile, the removal rates of Chemical Oxygen Demand (COD) achieved 76% under the optimal experimental conditions. In addition, Li et al. [114] fabricated Ag nanoparticle-decorated self-floating porous black  $\text{TiO}_2$  foams (FBTFs) by facile wet-impregnation and high-temperature surface hydrogenation strategy. The small Ag nanoparticles

with diameter of 3–4 nm were decorated on the surface of FBTFs uniformly, which extended the photoresponse to visible-light region and showed obvious surface Plasmon resonance (SPR). The Ag-FBTFs further exhibited excellent solar-driven photocatalytic performance due to the enhanced SPR effect. Holdich et al. [115] produced a neoteric kind of floating photocatalytic composite particles through injecting lipids, sunflower oil and liquefied cocoa butter into  $\text{TiO}_2$  aqueous suspension and finally photocatalytic reaction proceeded on the surface of floating particles. In this research, the photocatalytic performance was revealed by the decolorization of the dye indigo carmine solution. Membrane emulsification process was an important step to insure the generation of uniform floating composite particles with controllable median diameters size in a range from 80 to 300  $\mu\text{m}$ . Moreover, when composite particles were prepared by cocoa butter with hexane, silver nitrate and  $\text{TiO}_2$ , the optimal rates of decolorization were found at the surface coverage range of 60–80%. Similarly, methylene blue in aqueous solution was extensively applied to test the photocatalyst performance as a target compound. Syoufian et al. [116] studied submicrometer-sized  $\text{TiO}_2$  hollow spheres which had an adjustable quality of shell thickness and void volume, the photocatalytic activity was evaluated by decomposing MB. They also reported that peroxydisulfate could be used as an electron scavenger, and the addition of peroxydisulfate increased photocatalytic degradation rate and gained optimal photocatalysis activity of  $\text{TiO}_2$  hollow particles at a dose of 10 mM. Their results demonstrated that the photocatalytic activity was significantly enhanced by the utilization of peroxydisulfate.

The novel non-immobilized floating photocatalyst will have vital practical applications in fields of natural environment and also provide new insights for producing more photocatalytic materials with excellent characteristics.

#### 4. Summary and prospects

In summary, the applications of floating photocatalyst using different kinds of supports have been reported in literatures but it still remains in laboratory or pilot-plant scale, without industrialization. We summarize that the various carriers can be used to fabricate floating photocatalyst no matter it is immobilized or non-immobilized and analyze the preponderance of photocatalyst from the structural point of view. Meanwhile, in order to give readers a better understanding of the review, the condition using floating photocatalyst have been described in detail. As the core of floating photocatalyst,  $\text{TiO}_2$  have attracted more attention. As typical photocatalysts, the floating  $\text{TiO}_2$ -based photocatalysts immobilized or non-immobilized, have promising future. Although the most of dedicated work and researches focus on



**Fig. 13.** A. Schematic illustrating the formation process of self-floating amphiphilic macro-mesoporous black TiO<sub>2</sub> foams. B. SEM (a, b), TEM (c), HRTEM image (d) and digital photos (e, f, g) of the self-floating amphiphilic macro-mesoporous black TiO<sub>2</sub> foams (T600). The inset of (c) is the corresponding selected-area electron diffraction pattern. The white arrows of (c) point to mesopores. Reprinted with permission from Ref. [109].

immobilized floating photocatalyst, it is expected to be replaced by non-immobilized floating photocatalyst since the synthesis is simple, straightforward and ordinary.

In the domain of photocatalyst degradation of contaminant, some significant troubles which can affect large-scale practical applications of floating TiO<sub>2</sub>-based photocatalyst need to be urgently solved. The

appropriate carrier selection and TiO<sub>2</sub> modification are crucial for application to degrade pollution in industrial scale. In the future, the following aspects should be considered to enhance the performance of floating TiO<sub>2</sub>-based photocatalyst: (1) Novel, excellent floating photocatalyst supports need to be explored. (2) Adhesion of catalysts to the surface of the carrier must be intensified because it is the key to down-

to-earth applications of the photocatalyst. (3) Floating photocatalysts with visible light and/or NIR response require to be focused on. (4) Other floating semiconductor-based photocatalyst need to be explored that satisfied with practical applications. (5) Many significant, fulfilling and meaningful studies contribute to the structure and production methods should pay more attention. (6) Some advanced techniques especially in-situ ones should be developed to reveal the photocatalytic mechanism. Although the road is bumpy, the future of floating  $\text{TiO}_2$ -based photocatalyst is promising with the deepening of the research. This review that summarized the recent development and the understanding of floating  $\text{TiO}_2$ -based photocatalyst will provide new insights for designing and fabricating other high-performance floating photocatalytic materials.

## Conflict of interest

The authors declare no conflict of interests.

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